ON PRECAMBRIAN FRESHWATERS IN SOUTHERN ONTARIO

May, 1978



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EFFECTS OF ACIDIC PRECIPITATION ON

PRECAMBRIAN FRESHWATERS IN SOUTHERN ONTARIO

running head - Acidification of Lakes in Ontario

key words - acidification, buffering capacity, aluminum, manganese, precipitation

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PREFACE

The Limnology Unit of the Ministry of the Environment is conducting a number of studies dealing with acidification of lakes and rivers. This report describes recent studies (1976-78) pertaining to the effects of acidic precipitation on the Precambrian lakes of southern Ontario. An earlier report "Acidic Precipitation in South-Central Ontario: Recent Observations" released in September, 1977 outlined preliminary findings.

The contents of this report were presented at the Great Lakes Conference in Windsor, May, 1978.

ABSTRACT

The pH of precipitation falling on the Precambrian Shield of south-central Ontario averages 4.0 - 4.2, as low or lower than that of precipitation in areas of the world with recognized problems of acidification of freshwaters. The area is underlain by bedrock of low solubility with a thin glacial overburden and consequently many lakes have low buffering capacities. As a result, some lakes and streams have had their pH's reduced by acidic precipitation, especially during spring runoff and after storm events. The pH of some lakes is 5.0 - 5.5, a level at which the reproductive success of certain fish species is impaired. Other problems which may be related to the input of acidic precipitation are discussed.

INTRODUCTION

Recent evidence has demonstrated that the average pH of precipitation in southern Ontario is 4.0 - 4.2 (Dillon et al. 1978). Precipitation collected in this area is as acidic or more acidic than that collected near Sudbury, Ontario, southern Scandinavia and the north-eastern U.S.A., areas where acidification of freshwaters has been documented (Conroy et al. 1975, Gjessing et al. 1976, Schofield 1976). Because most of southern Ontario is underlain by Precambrian bedrock that can provide very little buffering capacity for streams and lakes, we have attempted to determine whether any freshwaters in this area are currently being affected by acidic precipitation.

This paper summarizes aspects of the precipitation chemistry studies for 1976 - 1978 and describes preliminary findings regarding lake and stream acidification in Precambrian areas of southern Ontario.

METHODS

Bulk precipitation is defined as that collected in a continuously open collecting device, while event or "wet only" precipitation is that collected in an automatic moisture-activated collector that is open only during periods of precipitation.

Precipitation collection techniques, lake and stream sampling and chemical methodologies have been previously described (Dillon et al. 1978). Aluminum and manganese were measured on unfiltered water samples and the results, therefore, include the colloidal and particulate as well as the dissolved fraction. Sediment cores were taken with a Wildco B Gravity Type corer and sectioned manually into 1 cm. slices.

Dry weights were obtained after 48 - 72 hr. at 110°C.

A description of the study locations was given by Dillon \underline{et} \underline{al} . (1978) and Jeffries et al. (1978).

RESULTS AND DISCUSSION

a. Precipitation chemistry

The pH's of bulk and event or "wet only" precipitation collected for varying periods of time at 9 stations on the Precambrian Shield and 4 stations to the south are reported in Table 1. The station mean pH's of bulk precipitation varied between 4.11 and 4.26 on the Shield and between 4.58 and 5.44 to the south of the Shield while those of event samples were 4.03 - 4.30 and 4.35 - 4.60 respectively. These findings are summarized in Table 2 along with results from other parts of the world.

These data show that on the Shield areas of southern Ontario, bulk precipitation is as acidic (overall mean pH of 4.17) as "wet only" precipitation (overall mean pH of 4.15), whereas to the south of the Shield, bulk precipitation is less acidic than "wet only" precipitation. Therefore, entrained material on the Shield (soil particles, etc.) does not provide buffering capacity for precipitation. Bulk precipitation falling on the Shield region of southern Ontario is more acidic than that collected off the Shield and more acidic (by about 40% when converted to hydrogen ion content) than that collected near Sudbury, Ontario. It is as acidic as that collected in the N.E. U.S.A. by Likens et al. (1975) and more acidic than that falling in Scandinavia (Dovland et al. 1976), areas where serious problems of lake and stream acidification already exist. Approximately 25% of bulk and event samples collected on the Shield region of southern

TABLE 1: Volume-weighted hydrogen ion content (as pH) of bulk (B) and event (E) precipitation samples collected on the Precambrian Shield (Stations 1-9) and south of the Shield (#10-13), n is the sample size.

	Station	Fraction	Period(s)	n	Mean pH	Range
1.	Carnarvon	В	August '76 - February '78	41	4.11	3.40 - 6.44
		E	September '76 - Apr-Nov. '77	29	4.14	3.23 - 6.09
2.	Eagle Lake	В	August '76 - January '78	37	4.26	3.91 - 6.88
		Ε	AugSept.'76 , May-Oct.'77	31	4.22	3.81 - 6.30
3.	Vankoughnet	В	July '76 - January '78	38	4.16	3.78 - 4.90
		E	April '76 - September '76	16	4.30	3.93 - 7.70
4.	Gullfeather	В	July '76 - October '77	24	4.23	3.83 - 5.80
5.	Dorset	В	November '76 - April '77	16	4.12	3.34 - 5.80
		Е	Nov.'76-Apr.'77 , Sept.'77-Jan.'78	35	4.03	2.97 - 5.93
6.	Red Chalk Lake	В	Aug. '76 - October '77	24	4.22	3.80 - 6.39
		E	Aug-Sept.'76 , May-Aug.'77	13	4.18	3.92 - 4.73
7.	Harp Lake	В	June '76 - October '76	6	4.17	3.69 - 4.36
		E	June '76 - October '76	9	4.38	4.07 - 5.36
8.	Harp Raft	В	August '76 - January '78	25	4.13	3.55 - 4.78
		Е	May '78 - October '78	12	4.19	3.88 - 4.46
9.	Grundy Lake	В	May '77 - September '77	8	4.26	4.02 - 6.36
		Е	May '77 - September '77	8	4.15	4.00 - 4.70

Table 1: Continued....

Station	Fraction	Period(s)	n	Mean pH	Range
10. Sibbald Park	В	July-Sept.'76 - May-Sept.'77	16	4.58	3.83 - 7.69
	E	May-Sept.'76 , May-Sept.'77	27	4.42	3.80 - 7.41
11. Madoc	В	September '76 - October '76	2	5.79	5.50 - 6.21
	E	May '76 - October '76	9	4.35	3.98 - 6.71
12. Silver Lake	В	July-Oct.'76 , May-July '77	10	5.44	4.84 - 6.70
	E	July-Oct.'76 , May-July '77	10	4.51	4.03 - 6.36
13. Tweed	В	May '77 - October '77	13	4.75	4.13 - 7.01
	E	May '77 - October '77	13	4.60	4.15 - 7.26

Table 2. Average pH of bulk and event precipitation in southern Ontario and at other locations experiencing acidification of freshwaters

	Bulk	Event
S. Ontario (on-shield)	4.11 - 4.26	4.03 - 4.30
S. Ontario (off-shield)	4.58 - 5.44	4.35 - 4.60
Sudbury	4.21 - 4.43	
N.E. USA 1	4.03 - 4.21	
Scandinavia ²	4.2 - 4.5	

¹Likens <u>et al</u>. (1975)

 $^{^{2}}$ Dovland et al. (1976)

Ontario had pH's of <4.0 (ie. contained more than 100 μ eq l⁻¹ of hydrogen ion).

The implications of these findings to the freshwaters of southern Ontario are discussed in the following sections.

b. Buffering capacities of lakes and watersheds

The ability of Precambrian lakes to neutralize acidic inputs, largely dependent on their ${\rm CO_3}^=$ - ${\rm H2CO_3}^-$ - ${\rm H_2CO_3}$ buffering system, is expressed in terms of alkalinity. Total "inflection point alkalinity" is defined as the amount of acid required to lower the pH of a water sample from the ambient level to that of the ${\rm H_2CO_3}$ - ${\rm HCO_3}^-$ inflection point. The inflection point is variable, depending on the total ionic content of the water. If the alkalinity titration is allowed to proceed to an arbitrarily defined endpoint (usually pH 4.5), the result is defined as "total fixed endpoint alkalinity". Both are expressed as either meq 1^{-1} or mg ${\rm CaCO_3}$ 1^{-1} (50 mg ${\rm CaCO_3}$ 1^{-1} = 1 meq 1^{-1}).

Titration curves for Red Chalk and Clear Lakes, two Precambrian lakes in Haliburton are shown in Fig. 1. For comparison, titration curves for Glen Lake, a lake in Haliburton with moderately hard water, and acidic Lumsden Lake in the La Cloche Mountains south of Sudbury (Beamish and Van Loon 1977) have been included. Red Chalk and Clear Lakes have buffering capacities closer to that of acidic Lumsden Lake, and much lower than hardwater Glen Lake.

Lakes in Precambrian areas commonly have low buffering capacities. 14 of 15 lakes included in our studies in this area have total inflection point alkalinities of <200 μ eq l⁻¹, with some as low as 10 μ eq l⁻¹ (Dillon et al. 1978). Ryder (1964) surveyed 310 lakes in Ontario and delineated large areas of poorly buffered waters (Fig. 2). His alkalinity

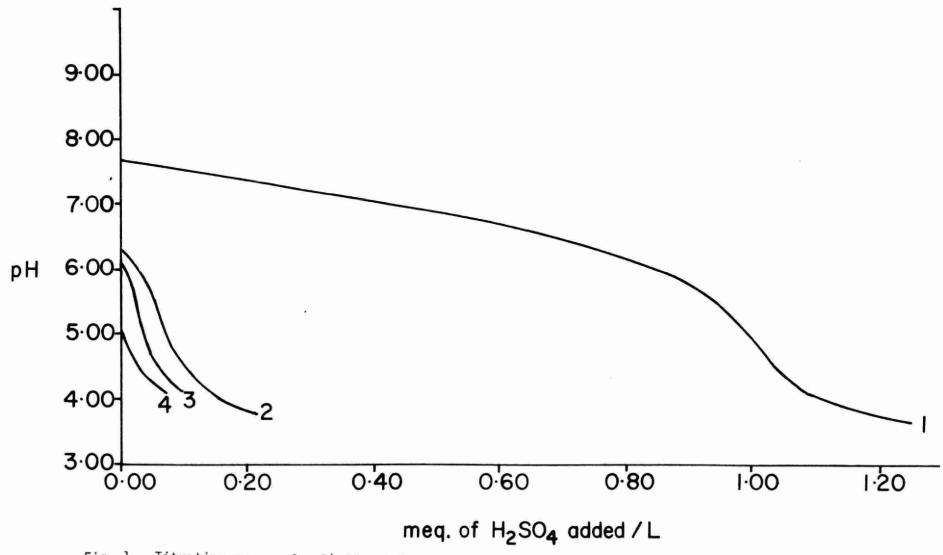
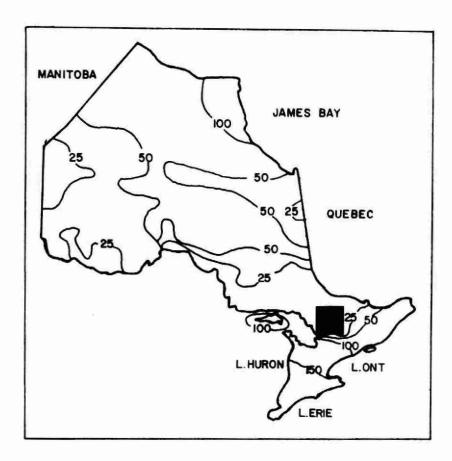


Fig. 1. Titration curves for 1) Glen Lake, a moderately hard water (alkalinity 0.98 meq 1⁻¹) lake on Precambrian sediments; 2) and 3) two of the Precambrian Shield Lakes studied in Haliburton-Muskoka, Red Chalk and Clear respectively, and 4) Lumsden Lake, an acidified lake in the La Cloche area (Beamish and Van Loon 1977).



ONTARIO TOTAL ALKALINITY ISOPLETH MAP

(mean concentration)

Fig. 2. Total alkalinity isopleths for Ontario lakes (from Ryder 1964). Based on a survey of 310 lakes. The study area is indicated by the shaded area.

values are total fixed endpoint values (pH endpoint about 4.5) and may be overestimates for Precambrian lakes because the inflection point of the alkalinity titration commonly occurs at pH 4.7 - 5.2 (rather than 4.5) in these dilute water bodies (Dillon et al. 1978).

Using precipitation and lake alkalinity data, it is possible to calculate the approximate length of time necessary to exhaust a lake's buffering capacity, ignoring renewal from the watershed. For example, a lake of mean depth 10 m having 50 μ eq l⁻¹ alkalinity has a total buffering capability of 500 meq m⁻², enough to withstand 5-7 years of precipitation of average annual depth 1.0 m and pH 4.14 (\approx 70 μ eq H⁺ l⁻¹). By varying alkalinity and mean depth, it can be seen that most Precambrian lakes themselves have 1-30 years of buffering capacity.

The soils and bedrock of a watershed provide considerable basic material in most cases. However, some watersheds may have had little neutralizing capacity or have already exhausted this capacity. The watershed of Red Chalk Lake may be divided into 4 subwatersheds, three of which (#1, #3, #4) have overburdens made up primarily of shallow till (Fig. 3). The mean annual pH of these streams in 1976 - 1977 was 6.0 (#1), 6.2 (#3) and 6.2 (#4) with colour of 47, 31 and 116 Hazen units respectively. The 4th stream has a mean annual pH of 4.5 and a colour of 114 Hazen units. Its watershed is made up of exposed bedrock and peat over bedrock with little surficial till. This type of overburden is not capable of buffering the acidic precipitation input.

Buffered watersheds may be inefficient at neutralizing acidic precipitation during storm events. Following a 2 cm. rainfall in July 1977, the H^{\dagger} content of Red Chalk stream #3 increased by a factor of 10 within

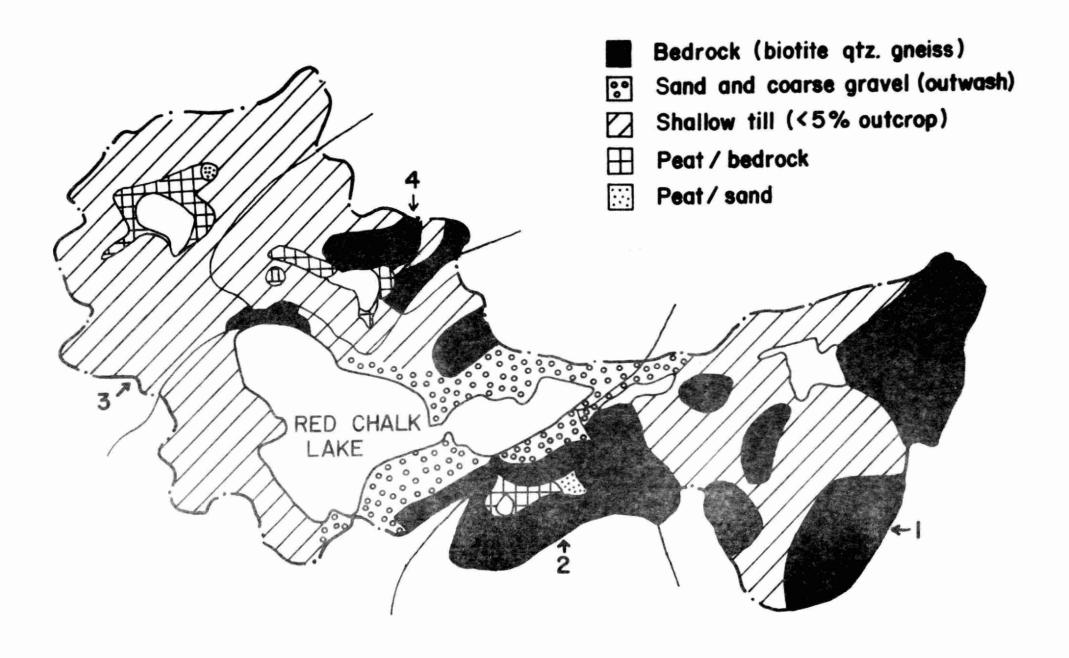


Fig. 3. Surficial geology of Red Chalk Lake's watershed.

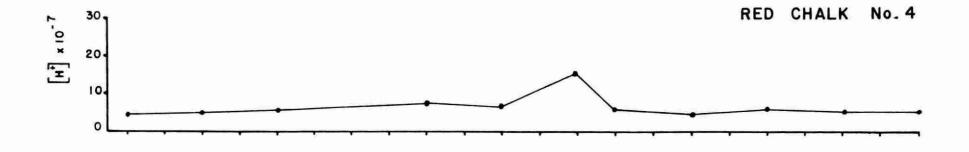
hours while that of stream #4 doubled (Fig. 4). Thus, even watersheds with residual buffering capacity may not be able to supply it fast enough to offset the low pH of precipitation during storm events.

Although it is the geochemistry and geomorphology on a microscale that determines a watershed's ability to buffer acidic precipitation, areas underlain by Precambrian bedrock with little or no surficial deposits (Fig. 5) must be regarded as being susceptible to the continued input of acidic precipitation. The areas identified in Ontario are geologically similar to the affected areas in the northeastern U.S.A. and in Scandinavia.

c. Current effects of acidic precipitation

Some lakes and rivers in southern Ontario are currently showing the effects of acidic precipitation inputs. A survey of 26 small, readily accessible lakes in Muskoka-Haliburton in January-March 1978 demonstrated that 85% had total inflection point alkalinities <100 μ eq 1⁻¹, while 35% had <40 μ eq 1⁻¹ (Fig. 6). The majority of lakes had pH's between 5.5 and 6.0 (0-5 m composite sample) with some as low as 4.5 - 5.0. If 3 dystrophic lakes (colour 70 Hazen units due to organic acids) are eliminated from the set of 26, 17% of the remaining lakes had pH's in the range 5.0 - 5.5. Reproduction of certain fish species may be impaired at these levels (Beamish 1976). Because organic acids were low in these lakes and because there are no point discharges of industrial effluents, it must be concluded that these lakes have been acidified by atmospheric inputs.

Although very few lakes with useful background chemical data exist, one exception is Clear Lake in Haliburton, studied in 1967 by Schindler and Nighswander (1970). Total inflection point alkalinity in 1967 ranged



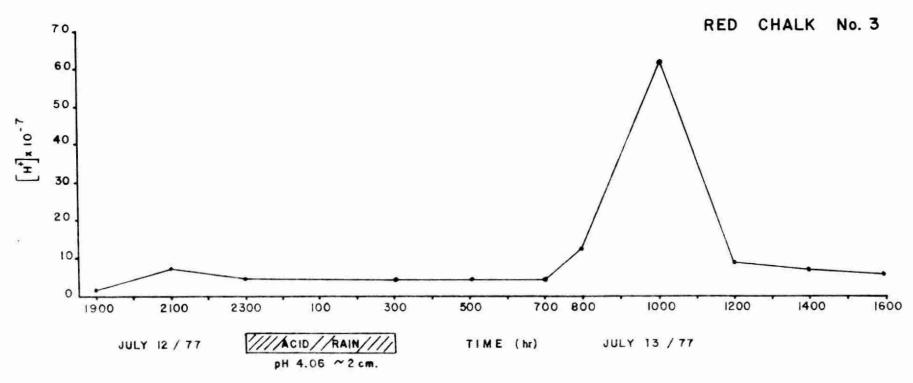


Fig. 4. Hydrogen ion content of streams draining Red Chalk sub-watersheds 3 and 4 showing effects of a 2 cm rainfall (pH 4.06) between 11:00 pm July 12/77 and 3:00 am July 13/77.

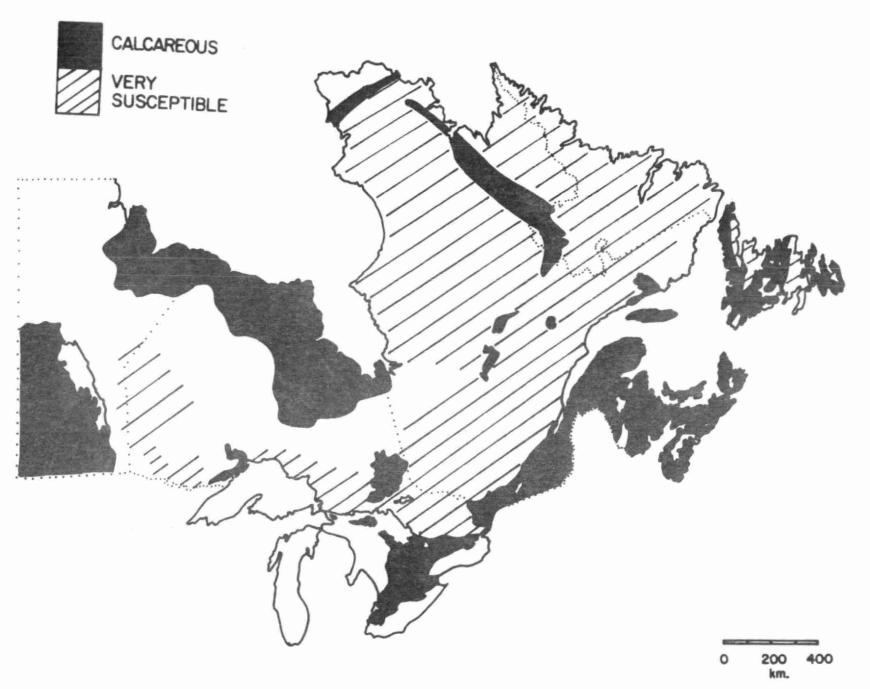


Fig. 5. Susceptibility to acidification of freshwaters and watersheds in eastern Canada (from Kramer 1976).

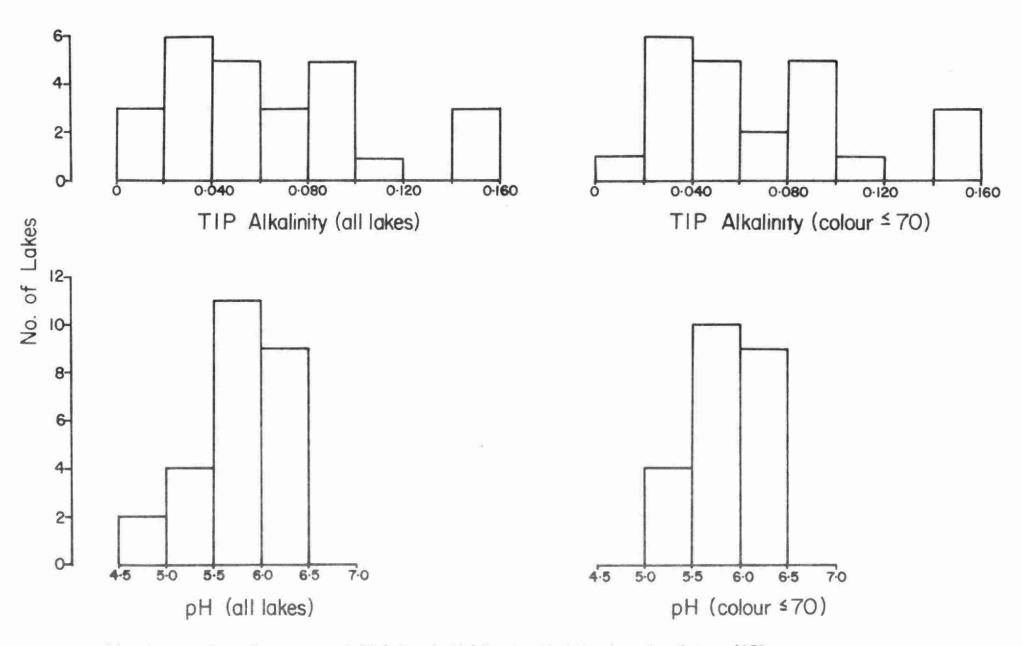


Fig. 6. Results of a survey of 26 lakes in Haliburton-Muskoka done in winter, 1978. Alkalinity is in meq 1^{-1} . 85% of the lakes had alkalinities of <0.10 meq 1^{-1} , while 17 lakes had pH <6.0, including 14 that are not dystrophic.

from 30 - 50 μ eq 1⁻¹. We measured total inflection point alkalinity in 1977 to be 2 - 15 μ eq 1⁻¹, an average reduction of about 75% over the 1967 figure.

Manganese and aluminum are good indicators of watershed acidification since they are readily removed from soils by acidic precipitation and are naturally low in Precambrian lakes. Our study lakes in Haliburton (Table 3) have total Al levels (49 μ g l⁻¹) that are midway between a group of non- or slightly affected Norwegian lakes of mean pH 6.4 and an affected group with mean pH of 5.40. Sudbury area lakes that are of intermediate pH (\approx 5.5) have approximately the same Al concentrations. Background Al levels are unknown but are probably in the neighbourhood of 2-10 μ g l⁻¹.

Manganese levels ($\simeq 50~\mu g~l^{-1}$) are considerably higher than background (3 $\mu g~l^{-1}$ at ELA, in northwestern Ontario). Beamish (1976) found that acidified lakes in the Killarney area had Mn concentrations >200 $\mu g~l^{-1}$, while our seriously contaminated Sudbury lakes were similar. The less affected but still acidic Sudbury lakes had levels only slightly greater than those in Haliburton.

The snowpack of all watersheds we have studied in Haliburton-Muskoka contained considerable amounts of acidic material. For example, the pH of the snowpack of Red Chalk Lake ranged from 3.96 - 4.58 in January - February 1977 (Fig. 7). A comparison of stream pH during spring snowmelt and mean annual pH is shown for 10 streams in the area in Table 4. The percent increase in [H⁺] ranges from 0-530%, with most figures between 100-200%. Data for Fawn Lake, Muskoka, demonstrate that the acidic meltwater can reduce lake pH, especially in surface waters (Table 5). The pH of the top 5 m of Fawn Lake dropped from 5.8 (fall composite sample 1975) to 4.2 (March 1976), a level which causes reproductive impairment in many fish and is toxic to some (EIFAC 1969).

Table 3. Aluminum and manganese concentrations (mg m⁻³) in Haliburton lakes compared to acidified and non-acidified lakes in other parts of the province and Scandinavia

Location	# lakes	Description	[A]	[Mn]
Haliburton	14		49	51
E.L.A.1	102	circum-neutral		3
Killarney ¹	2	pH 4.8 - 5.0		240
Sudbury	5	pH 4.0 - 4.6	280-380	100-300
Sudbury	2	pH 5.5	69	67
Norway ²	52	pH 6.4	28	
Norway ²	20	pH 5.4	86	
Norway ²	26	pH 4.7	200	

¹Beamish (1976)

²Gjessing <u>et al</u>. (1976)

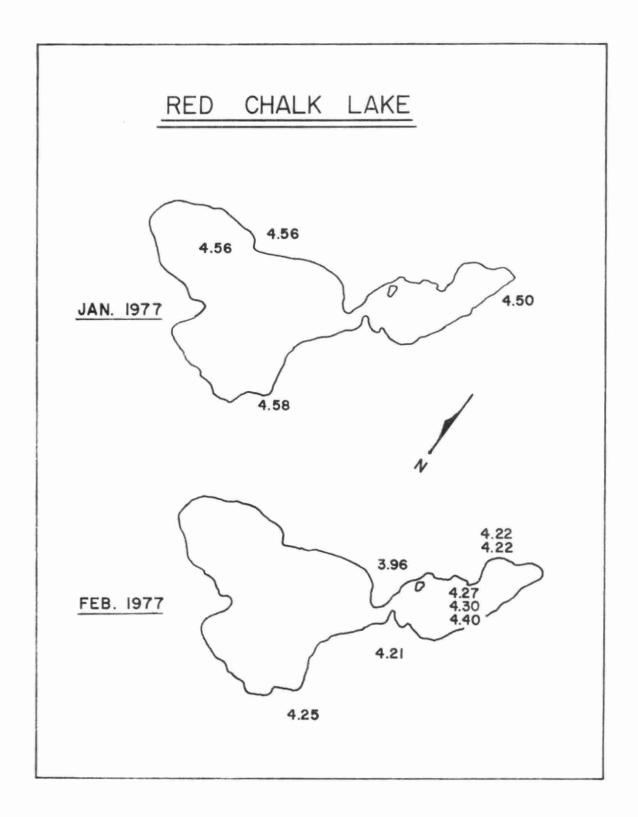


Fig. 7. pH of snow cover on Red Chalk Lake and its watershed at the end of Jan. and Feb. 1977.

Table 4: Mean stream pH*; late March and the remainder of the year.

	1976			1977		
Stream	Late March (n)	Remainder (n)	% Diff. [H ⁱ] [†]	Late March (n)	Remainder (n)	% Diff [H ⁺]
Blue Chalk #1	6.1(2)	6.1(18)	0	6.2(3)	6.2(24)	0
Red Chalk #1	5.7(2)	6.0(31)	100	5.7(4)	6.0(32)	100
Red Chalk #3	5.9(2)	6.2(30)	100	5.8(4)	6.2(33)	151
Red Chalk #4	5.7(2)	6.2(29)	216	5.7(4)	6.2(34)	216
Harp #3	5.7(3)	5.9(30)	58	5.4(5)	5.9(30)	216
Harp #3A	-	-	-	5.9(4)	6.1(34)	58
Harp #4	6.1(3)	6.5(37)	151	5.9(5)	6.2(33)	100
Harp #5	5.4(4)	5.7(26)	100	5.1(5)	5.6(32)	216
Harp #6	5.6(3)	5.8(28)	58	5.8(5)	6.0(31)	58
Chub #1	5.0(1)	5.8(22)	530	4.8(2)	5.5(35)	401

^{*} Mean pH = $-\log_{10} \left[\left(\sum_{i=1}^{n} \operatorname{antilog} \left(-pH_{i} \right) \right) /_{n} \right]$

^{† %} Diff.[H+] = $\frac{\text{antilog (-pH_{March})- antilog (-pH remainder)}}{\text{antilog (-pH_{remainder})}} \times 100$

Table 5: pH of Fawn Lake, Muskoka in the fall of 1975, during snowmelt in 1976, and in the summer of 1976.

Time	Depth (m)	рН
Fall, 1975	Surface to bottom	5.8
March, 1976	0-5	4.2
à.	5-10	4.8
	10-bottom	5.3
Summer, 1976	Surface to bottom	5.8
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d. Related Problems

Copper, nickel and lead levels are elevated in near-surface sediments in the 15 lakes we have studied in Haliburton-Muskoka (eg Fig. 8 for Red Chalk Lake). The fact that heavy metal inputs to lakes have increased in recent times has also been documented in the N.E. U.S.A. (Galloway and Likens 1977) and Scandinavia (Henriksen and Wright 1978). The significance of this to aquatic organisms is uncertain, but it is possible that as lake buffering capacities and pH's drop because of acidic precipitation, resolubilization of toxic heavy metals will occur.

The mercury content of walleye as a function of fish length is shown in Fig. 9 for lakes of low alkalinity (<15 mg CaCO₃ l⁻¹, or 300 µeq l⁻¹) and of high alkalinity. These data were collected from a large number of lakes across Ontario and represent analyses of more than 2000 fish. They indicate that for walleye, fish of a given size have higher mercury content in lakes of low alkalinity than those in higher alkalinity waters with an arbitrary boundary of 15 mg CaCO₃ l⁻¹. Although this implies no cause-effect relationship, it does suggest that, should these results be related to the mechanism for mercury cycling or uptake, a decrease in buffering capacity of some of these lakes may lead to increased mercury levels in their fish populations.

These 2 related problems will be discussed in detail elsewhere.

e) Summary

- i) Precipitation falling on southern Ontario is as acidic or more acidic than that falling on areas of the world identified as having severe problems related to acidification of freshwaters.
- ii) The majority of the lakes in this area have very low buffering capacities, and the surficial deposits in many watersheds have

RED CHALK LAKE (µg/g dry wt)

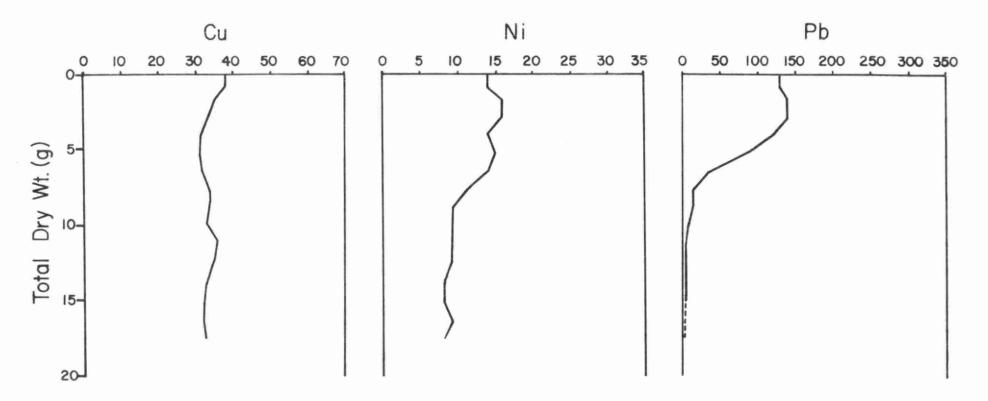


Fig. 8. Concentration of copper, nickel and lead as a function of cumulative dry weight in the sediments of Red Chalk Lake. Nickel and lead levels are elevated in recent deposits (the last few decades).

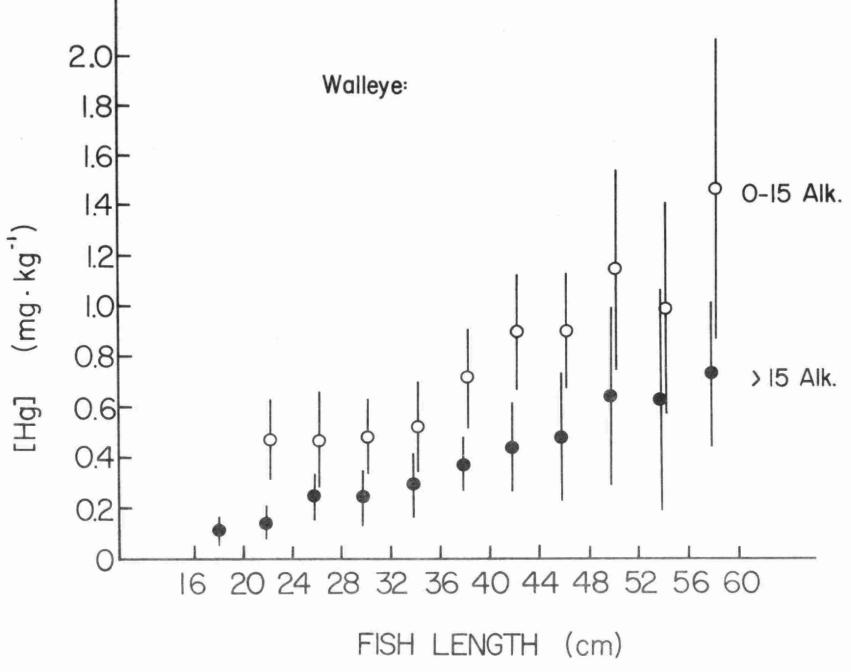


Fig. 9. Concentration of mercury in walleye (Stizostedion vitreum vitreum (Mitchill)) as a function of fish length in two groups of lakes, one of 21 lakes with alkalinity <15 mg CaCO $_3$ l $^{-1}$ (0.30 meq l $^{-1}$), the other 31 lakes having >15 mg CaCO $_3$ l $^{-1}$. A mean concentration was taken for each size class in each lake and an overall mean taken for a given size class for all lakes.

- limited, in some cases negligible capability of neutralizing the precipitation.
- iii) There are presently lakes and streams in Haliburton-Muskoka that have had their pH's reduced by acidic precipitation, especially during spring runoff and after storm events. The pH's of some freshwaters in the area may be low enough to impair the reproductive success of certain species of fish.
- iv) Trace metal levels are elevated in recently deposited lake sediments and other lake problems such as increased mercury content in fish may become more pronounced as lake alkalinities and ultimately lake pH's decline due to acidic precipitation.

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